

The diffusion annealing step affected the composition of the various layers of the coating little, regardless of the length of the treatment time.

On samples of the same type, isothermal oxidation tests were performed at 1450° C.

Thermogravimetric analysis showed that this type of coating has better behavior than known coatings.

Oxidation takes place slowly and conditions rapidly become linear. Thus, after 10 hours, mass variation was slightly less than 1 mg/cm².

EXAMPLE 6

Two alloys liable to self-ignition because of a low ignition temperature and high combustion heat, were tested. To this end, samples were made firstly of a niobium based alloy and secondly of a titanium based alloy.

The niobium based alloy samples had the same composition as in Example 1, and the coating layer having a thickness of 80 μm was prepared in identical manner: it was brushed on and then subjected to heat treatments.

The samples of titanium based alloy used the alloy known as TA6V and they were covered in a layer having the following composition:

Ti: 30%

Mo: 10%

Y: 0.3%

B: 2.0%

Cr: 4%

Si: balance needed in order to reach 100%.

However, the composition was deposited in two different ways:

deposition by detonation spraying, giving a coating having a thickness of 40 μm to 60 μm; and

deposition by cold supersonic spraying, giving a coating thickness of about 10 μm.

There was no subsequent heat treatment.

In all cases, the samples were disks having a diameter of 13 mm and a thickness of 6 mm, and they were coated on one face.

The compatibility test used was an adiabatic compression test under oxygen (O₂) at high pressure in application of the standard NF E 29-690.

General conditions were as follows:

initial O₂ temperature: 60° C.

maximum O₂ pressure: 30 MPa

number of cycles: 20.

For the batch of niobium-based alloy samples and for both batches of titanium-based alloy samples, no combustion was observed. It should be emphasized that rapid adiabatic compression of gaseous oxygen gives rise to very great heating of the test pieces, such as 1420° C. at the final pressure of 30 MPa.

The ignition temperature of unprotected titanium alloy under high oxygen pressure is normally less than 600° C.

The coating is therefore entirely effective in providing protection against the risk of self-ignition.

EXAMPLE 7

An aqueous suspension was made of a mixture of powders having the following composition (percentage by weight):

Ti: 30%

Mo: 10%

Cr: 0.2%

Y: 0.5%

B: 2.0%

Fe: 7%

Si: balance needed in order to reach 85%. The mixture was therefore lacking 15% silicon.

A composite material test piece made of C—SiC (carbon fiber reinforcement and SiC matrix) having a porosity of about 10% was used. It was impregnated by being dipped under a vacuum, filling its pores and simultaneously coating the surface of the material with the composition, and it was then baked at 120° C. for half an hour to eliminate the water.

In a vacuum furnace, elemental silicon was heated in a crucible to a temperature of 1440° C. The silicon was then liquid.

The test piece prepared in the above manner was then immersed in the liquid silicon, with the liquid silicon thus penetrating into the pores, and finally reacting with the powder present so as to make the initial composition up to 100%.

A composite material was thus obtained that was protected both on the surface and in bulk by the general composition as described in Example 2.

We claim:

1. A product made of refractory material protected against oxidation by a coating formed at least on the surface of the material and comprising a refractory phase interpenetrated by a healing phase, characterized in that the refractory phase is formed mainly by the refractory silicide $Ti_{(0.4-0.95)}Mo_{(0.6-0.05)}Si_2$, and the refractory phase has a branching microstructure forming an armature within which the healing phase is distributed, which healing phase is constituted by a eutectic formed mainly of unbound silicon, of the silicide $Ti_{(0.4-0.95)}Mo_{(0.6-0.05)}Si_2$, and of at least the disilicide $TiSi_2$.

2. A product according to claim 1, characterized in that the healing phase further includes at least one disilicide $MeSi_2$, in addition to the $TiSi_2$, where Me is a metal taken from groups 3 to 8 of the periodic classification of the elements.

3. A product according to claim 2, characterized in that: the coating further includes a surface oxide film comprising silica obtained by oxidizing silicon contained in the coating;

Me is a metal selected from Mn, Fe, Co, and Ni;

the refractory material is selected from the group consisting of:

alloys of niobium, of tantalum, of molybdenum, of tungsten, intermetallic compounds and alloys containing dispersed oxide phases; and

aluminum, titanium, nickel, alloys thereof, and intermetallic compounds and alloys of the $TiAl$, Ti_3Al , $TiAl_3$, $NiAl$, Ni_3Al type, for which the coating performs an anti-ignition function on the other hand;

the refractory material is a composite material containing carbon;

the refractory material is a composite material selected from carbon—carbon and carbon—SiC composite materials.

4. A method of obtaining a product of refractory material that is protected against oxidation, according to claim 3, the method comprising the steps consisting in:

preparing a mixture containing powders having the following composition in percentage by weight:

Ti: 15% to 40%